Diffusion of TiN Into Aluminum Films Measured By Soft X-Ray Spectroscopy

T.M. Schuler[1], D.L. Ederer[1], N. Ruzycki[1], G. Glass[2], W. A. Hollerman[2], A. Moewes[3], M. Kuhn[4], and T. A. Callcott[5]

[1]Department of Physics, Tulane University, New Orleans, LA 70118
[2]Acadiana Research Laboratory, University of Louisiana at Lafayette, P.O. Box 44210, Lafayette, LA 70504,
[3]Center For Advanced Microstructures and Devices, CAMD at Louisiana State University, 6980 Jefferson Hwy., Baton Rouge, LA 70803. (current address: Department of Physics and Engineering Physics, University of Saskatchewan, Saskatoon, SK, S7N 5E2, Canada.
[4]Digital Equipment Corporation, 77 Reed Rd., Hudson, MA 01749. (current address: 2501 229th Ave., Hillsboro, OR 97124)
[5]Physics and Astronomy Department, University of Tennessee, Knoxville, TN 37996.

INTRODUCTION

The study of interactions between thin films has become a matter of increasing importance over the past few years as the demand for innovative materials has intensified greatly, most notably in microcircuit industry[1]. The manner in which thin films react with each other is an important consideration for the use of thin films in devices. The study presented here concerns the reactions on the interface between titanium nitride thin films and a film composed of 99% aluminum and 1% copper.

Titanium nitride (TiN_x) is a unique material because of its unusual combination of properties. Its basic structure is that of a face-centered cubic lattice. The properties attributed to TiN_x consist of a high level of hardness, high thermal conductivity, an immunity to wear and corrosion, chemical inertness, and a resistance to atomic diffusion within its matrix. These properties suggest a partially filled band and a chemical bond consisting of metallic, covalent, and ionic character simultaneously[2].

X-ray emission spectroscopy (XES) and x-ray absorption spectroscopy (XAS) are useful tools in measuring the electronic states of both bulk and thin film systems. Using these spectroscopic methods, one can examine the properties of the thin film/substrate interface in a non-destructive manner, and they can provide a probe of the interface that is atomic site-specific. The electronic structure of titanium, along with a variety of titanium compounds, has been extensively studied[2] by means of soft x-ray emission and absorption spectroscopy.

In this work we present data from XAS and XES measurements on titanium nitride thin films and their interaction with an aluminum/copper intermediate layer. We also use a model of the x-ray fluorescence intensity as a function of the exciting photon energy across the titanium $L_{2,3}$ absorption edge in TiN to discuss migration of Ti and N into the substrate. Our main point of interest in performing these experiments was whether a significant change in composition occurred in any of the materials at the interface, which could be attributed to either the preparation temperature or the presence of the other layers of the sample.

EXPERIMENT

The soft x-ray fluorescence and emission measurements were made at Beamline 8.0 of the Advanced Light Source located at Lawrence Berkeley National Laboratory, which is an

undulator beamline equipped with a spherical grating monochromator. A detailed description of the apparatus and experimental process is provided by Jia, *et al.*[3].

The sample consisted of 40 nm films of TiN mounted above and below the aluminum/copper film of thickness 550 nm. Measurements were taken on samples annealed at temperatures of $410^{\circ}C$ and $450^{\circ}C$ with the TiN over-layer present, then the over-layer was removed and the measurements were repeated in an attempt to reach the TiN sub-layer. The removal of the over-layer was accomplished by a selective wet chemical etch. Both the Al(Cu) and TiN films were sputter-deposited using an Al(Cu) or Ti target. In the case of the TiN films, nitrogen was introduced during the sputter deposition process.

RESULTS

We modeled the obtained fluorescence intensity from the titanium nitride cross section using transmission data calculated by the Center For X-Ray Optics (CXRO) at Lawrence Berkeley National Laboratory[4] as a starting point. We then applied the equation for the intensity developed by Jaklevic, *et al.*[5]. In our model we took the fluorescence yield of titanium to be one-tenth of that of nitrogen. This model, shown in Fig. 1, provides an excellent qualitative match to our data, as can be seen by comparing the titanium and nitrogen peaks in Fig. 1 with the data plots shown in Fig. 2.

In comparing the data taken from the three TiN samples, we notice several changes in the peak features. First of all, the near edge x-ray absorption fine structure (NEXAFS) for bulk TiN matches very well with the thin film of TiN (Fig. 2). Secondly, both N and Ti remain after the TiN over-layer is removed, when one should not observe either element. Thirdly, the NEXAFS structure at the N K-edge of the etched sample is very different than that of bulk TiN. Finally, we are led to the conclusion from our model comparison in Fig. 1 to Fig. 2(c), that the N and Ti diffuse into the Al to an extent that could be equivalent to a film of thickness 4.5 nm.

The emission at the N K-edge closely resembles that of the TiN bulk powder. The major difference occurs at the Ti $L_{2,3}$-edge. (Fig. 3(b)). In an attempt to explain the variation from TiN at the Ti L-edge, we compare our data to previous measurements on hexagonal aluminum nitride
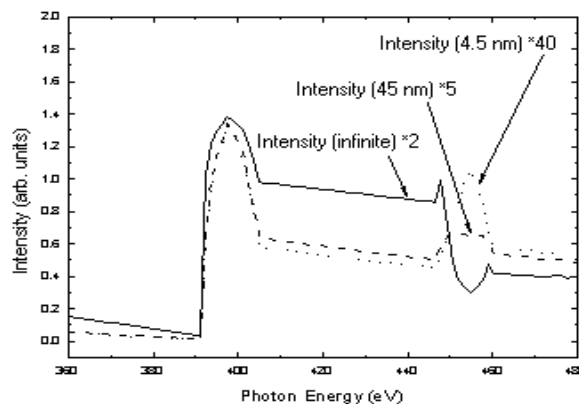
FIGURE 1. Adjusted model of fluorescence intensity of TiN sample accounting for self-absorption in titanium, assuming $Y_{Ti} = Y_N / 10$.
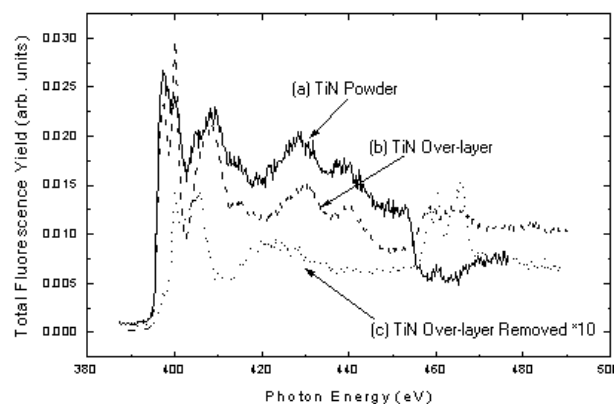
FIGURE 2. NEXAFS fluorescence measurements for fine structure of bulk TiN powder, plot (b) is that of our layered sample with the TiN over-layer present, and plot (c) shows our layered sample with the TiN over-layer etched away. The intensity of plot (c) has been multiplied by a factor of ten to allow for comparison with the other plots.

as reported by Lawniczak-Jablonska *et al.*[6] shown in Fig. 3. There is convincing agreement between the AlN data in Fig. 3(a) and the data from our sample with the TiN over-layer removed, shown in Fig. 3(b) which is a strong indication that the nitrogen from the TiN layer has diffused into the aluminum to form an AlN material.

Indirect evidence also suggests that titanium has diffused into the aluminum. Measurements taken at the Ti $L_{2,3}$-edge confirm the presence of titanium in the etched sample. The signal from the etched sample is weaker than that of the TiN over-layer by about a factor of five, whereas we would expect this signal to be reduced by a factor of 25 if the emission were coming from the TiN sub-layer. Therefore, we conclude that all of the emission measured at the Ti $L_{2,3}$-edge of the etched sample must be coming from the aluminum intermediate layer, implying that titanium has diffused into this layer as well as the nitrogen.

Figure 3. Our measurements performed on the sample with the TiN over-layer (a), compared with previously measured emission and absorption data (b) performed on hexagonal AlN. The N *K*-edge emission peaks (left) compare very well with the AlN measurements at that energy.
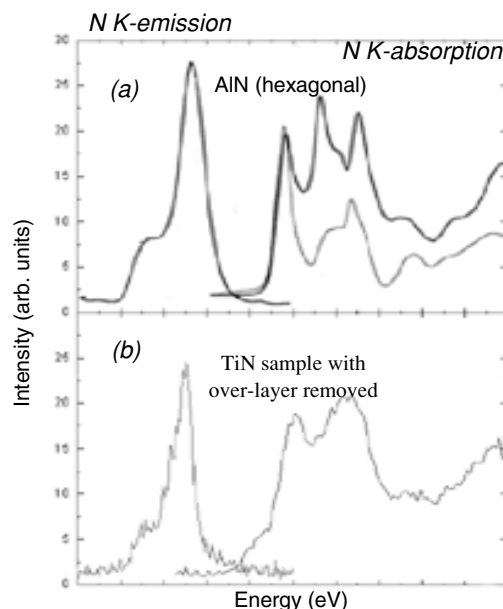
CONCLUSIONS

From our data analysis, we conclude that on our multi-layer sample the TiN thin film over-layer has electronic properties that are very similar to those of bulk TiN. We also found that when the TiN over-layer was removed, the aluminum layer below it changed in a manner closely resembling that of aluminum nitride. From this we conclude that the nitrogen from the TiN layers had diffused into the intermediate layer, which has been substantiated by RBS measurements. XES measurements indicate that titanium from the over-layer has also diffused into the aluminum. Our data on the etched sample also suggested that emission from the TiN sub-layer was probably not being detected.

REFERENCES

1. W. Monch, *Semiconductor Surfaces and Interfaces* (Springer, New York, 1993)
2. D. W. Fischer and W. L. Baun, J. Appl. Phys. **39** (1968), 4757.
3. J. J. Jia, T. A. Callcott, J. Yurkas, A. W. Ellis, F. J. Himpsel, M. G. Samant, J. Stohr, D. L. Ederer, J. A. Carlisle, E. A. Hudson, L. J. Terminello, D. K. Shuh, and R. C. C. Perera, Rev. Sci. Instrum. **66** (1995), 1394.
4. B. L. Henke, E. M. Gullikson, and J. C. Davis. *X-ray interactions: photoabsorption, scattering, transmission, and reflection at E = 50 – 30,000 eV, Z = 1-92,* Atomic Data and Nuclear Tables. 54(2) (1993), 181.
5. J. Jaklevic, J. A. Kirby, M. P. Klein, A. S. Robertson, G. S. Brown, and P. Eisenberger, Solid State Commun. **23** (1997), 679.
6. K. Lawniczak-Jablonska, T. Suski, I. Gorczyca, N. E. Christensen, K. E. Attenkofer, E. M. Gullikson, J. H. Underwood, D. L. Ederer, R. C. C. Perera, and Z. Liliental Weber, Phys. Rev. B **61** (2000), 16623.

Principal investigator: Dr. David L. Ederer, Department of Physics, Tulane University. Telephone: 504-862-8268. Email: dlederer@tulane.edu.